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Quantitative Separation of Asbestos in Environmental Samples

Arthur D. Little, Inc.
Cambridge, MA

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16. ABSTRACT

Evaluations were made of a novel approach for separating chrysotile asbestos from other particulate matter to improve the application and detection limit of a broad beam x-ray diffraction analysis method developed by the Naval Research Laboratory. The separation method is based on Selective Nucleation of Crystal Growth (SNCG) whereby treatment of a particulate sample with a special reagent results in the nucleation and growth of crystals along asbestos fibers but not on other matter. The fibers can be thereby increased substantially in mass, volume and density. The reagent previously developed for chrysotile asbestos consists of mixed salts of AgI and KI in ethylene glycol-acetone-water solution, with AgI crystals (density of 5.67 g/cm^3) being the decorating agent. Attempts to develop a comparable reagent for amphibole asbestos were unsuccessful. Minerals structurally or chemically related to chrysotile gave no reagent response except for moderate response by lizardite and slight response from antigorite. Mixed mineral samples consisting of known amounts of chrysotile and quartz were reagent-treated, resulting in AgI overgrowths of up to 25 μm in diameter. Separation of the decorated asbestos from quartz by a high density liquid with and without centrifugation and by Stokes settling were unsuccessful; recoveries of about 50 percent of both chrysotile and quartz were found in the separated fraction. Furhter work is required to improve the separation process.

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QUANTITATIVE SEPARATION OF ASBESTOS IN ENVIRONMENTAL SAMPLES

by

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FOREWORD

Environmental protection depends on efforts to detect, identify and quantify specific pollutants and to assess their effects. As part of this Laboratory's research to determine the relationships between emissions of pollutants from all types of sources and air quality, the Emissions Measurement and Characterization Division conducts studies to determine the chemical and physical nature of pollutants emitted to the atmosphere and develops methods and instrumentation for their measurement. The Division also develops state-of-the-art measurement methodology for the monitoring, regulation, and enforcement activities of the Environmental Protection Agency.

The limitations of current methods for quantitative analysis of asbestos in environmental samples are partly due to interferences and other difficulties posed by the presence of relatively large amounts of background material. Sample pretreatment resulting in removal of substantial amounts of the non-asbestos material should simplify many of the analytical problems. This report describes efforts to apply the technique of selected nucleation of crystal growth as a means for separating asbestos.

Alfred H. Ellison
Director
Environmental Sciences Research Laboratory

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ABSTRACT

Evaluations were made of a novel approach for separating chrysotile asbestos from other particulate matter to improve the application and detection limit of a broad beam x-ray diffraction analysis method developed by the Naval Research Laboratory. The presence of other particulate matter impedes electrostatic alignment of fibers required for the x-ray method. The separation method is based on Selective Nucleation of Crystal Growth (SNCG) whereby treatment of a particulate sample with a special reagent results in the nucleation and growth of crystals along asbestos fibers but not on other matter. The fibers can be thereby increased substantially in mass, volume and density. The reagent previously developed for chrysotile asbestos consists of mixed salts of AgI and KI in ethylene glycol-acetone-water solution, with AgI crystals (density of 5.67 g/cm^3) being the decorating agent. Attempts in this program to develop a comparable reagent for amphibole asbestos were unsuccessful. Low temperature ashing in an rf-generated oxygen plasma was found to be appropriate for removing organic matter from filtered air and water samples. Other minerals structurally or chemically related to chrysotile gave no reagent response except for moderate response by lizardite and slight response from antigorite which, together with chrysotile are serpentines. Mixed mineral samples consisting of known amounts of chrysotile and quartz were reagent-treated, with AgI overgrowths of up to 25 μm in diameter. Separation of the decorated asbestos from quartz by a high density liquid with and without centrifugation and by Stokes settling were unsuccessful; recoveries of about 50 percent of both chrysotile and quartz were found in the separated fraction. Further work is required to improve the separation process.

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SECTION 1

INTRODUCTION

Asbestos is known to be a carcinogen. Asbestos-related diseases are insidious, having a latency period of 20 or more years after exposure. Much of the data implicating asbestos are based on epidemiological studies of particular occupational groups. A clear dose-response relationship is non-existent at this time. It is known, however, that exposure in conjunction with cigarette smoking introduces considerable additional risk.

At present, no ambient air regulatory standards have been proposed by the EPA. However, in recognition of the accumulated medical evidence, asbestos has been defined as a hazardous air pollutant and regulations have been promulgated for the control and limitation of asbestos emissions from several point sources, including asbestos mills and associated roadways and manufacturing of various asbestos-containing commercial products. Other federal regulations have been adopted by OSHA that specify standards for occupational exposure to asbestos dust calling for an 8-hour time weighted average airborne concentration of asbestos dust not exceeding two fibers longer than 5 μm per milliliter of air. Fiber identification and counting for this standard is by phase contrast microscopy at approximately 400X.

Optical microscopy is limited in resolution to the wavelength of visible light. Therefore, any fibers having a width less than a few tenths of a micron will not be observed. Reliable measurements of all asbestos fibers in a sample require analysis by electron microscopy. EPA recently funded a program for the development of an optimum methodology for the measurement of airborne asbestos concentrations by electron microscopy[1]. However, because of the complexity of the method, relatively long analysis times, high cost and semi-quantitative results, the electron microscopy method is not suitable for routine measurement or monitoring of airborne and waterborne asbestos. As a result, in support of the EPA's need for a rapid survey technique, work was

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supported at the Naval Research Laboratory in which the feasibility of an x-ray diffraction technique was demonstrated for the direct quantitative measurement of small masses (as little as 0.2 μg) of chrysotile[2-4]. The method involves the electrostatic alignment of fibers and embedding them in a thin film for x-ray diffraction measurement. In applying this method to environmental samples, however, the presence of relatively large quantities of nonasbestos materials can (a) interfere with the fiber alignment step in the specimen preparation procedure and (b) adversely affect the limit of detection by increasing the background signal to unacceptably high levels.

As a result, the purpose of this study was the development of a procedure (or procedures) for separating asbestos from, or concentrating asbestos relative to, other materials in environmental samples (including airborne and waterborne samples and samples from rock quarrying and iron ore processing operations) with minimal and preferably negligible loss of asbestos fibers. The separation procedure(s) to be developed shall be applicable to the preparation of sample specimens amenable to the determination of the mass concentration of asbestos species present (e.g., chrysotile, crocidolite, tremolite, etc.) by bulk analytical techniques, particularly by a special x-ray diffraction technique described earlier[2-4]. Parameters to be considered in evaluating the effectiveness of the developed procedure(s) include (a) the degree of separation achieved, (b) the level of fiber loss, and (c) the amenability of purified or partially purified samples to analysis by the aforementioned x-ray diffraction technique.

Emmett Smith at Arthur D. Little, Inc has previously developed a detection method for chrysotile based on Selective Nucleation of Chrystal Growth (SNCG). When an environmental sample containing chrysotile is treated with an appropriate supersaturated solution, crystals of silver iodide nucleate and appear to grow selectively on the chrysotile fibers. The present program is directed to applying the SNCG methods to selectively decorate asbestos in the presence of other extraneous matter followed by separation on the basis of differences in size or mass. After separation, the silver iodide is dissolved and the isolated fibers used to prepare samples appropriate for the aforementioned x-ray diffraction method.

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The study described herein emphasized the development of a separation protocol for chrysotile and the identification of one or more SNCG reagents suitable for amphibole asbestos.

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SECTION 2

CONCLUSIONS

Experiments evaluating the SNCG procedure for separating asbestos from other particulate matter lead to the following conclusions:

- A range of compositions of AgI and KI in an ethylene glycol-acetone-water solution was found to be suitable as a SNCG reagent for chrysotile.
- A variety of related minerals were nonreactive to the reagent, except for partial reaction with lizardite and antigorite.
- The search for a SNCG reagent specific to amphibole asbestos varieties was unsuccessful.
- Low temperature ashing was found to be a suitable preseparation method for removing organic matter from filtered water samples, with chrysotile recoveries of 75 to 100 percent.
- Separation of reagent-treated chrysotile from quartz and from nonfibrous serpentinites was unsuccessful by Stokes settling or by high density liquid sink-float separation, both with and without centrifugation.

SECTION 3

RECOMMENDATIONS

Further experimental effort should be expended in separating the AgI decorated chrysotile asbestos from other coexisting particulate matter. In this respect, consideration should be given to

- Dilution of the reagent-treated material with the KI saturated solution to minimize particle impingement during Stokes settling, high density fluid sink-float and centrifugation.
- Particle surface modification with surfactants or charge modification substances to minimize particle agglomeration or attraction.
- Electrophoretic separation of the AgI-decorated chrysotile particles.
- Selective filtration, whereby the large (decorated) chrysotile fibers are captured on the filter whereas other particles pass through. This process would require an additional step to recover the particles from the filter.

It is still necessary to demonstrate the suitability of separated material for preparing aligned fiber x-ray samples.

Experiments should be designed to measure the improvement in x-ray detection sensitivity after chrysotile separation from extraneous matter as well as the loss of chrysotile due to the separation process.

If improvement in the x-ray sensitivity for chrysotile is realized, further effort should be made in identifying a SNCG reagent for the amphibole variety of asbestos.

SECTION 4

EXPERIMENTAL EVALUATIONS

SELECTIVE NUCLEATION OF CRYSTAL GROWTH (SNCG)

Background

In a research project sponsored by Arthur D. Little, Inc. starting in 1973, it was discovered that cyrstals of silver iodide could be grown on chrysotile fibers, resulting in an optical "magnification" of such fiber diameters by as much as five-fold. The growth was achieved from a supersaturated solution of AgI prepared in a manner first suggested by Vonnegut[5]. AgI is readily soluble in ethylene glycol-acetone mixtures containing KI. Upon evaporation of the acetone from such solutions, a metastable supersaturated AgI solution is obtained.

From these prior experiments concerned with the microscopic detection of chrysotile it was determined that useful concentrations of AgI and KI ranged from 25 g/L each to 5 g/L each for a 1:1 mixture of ethylene glycol and acetone. At the high concentrations (10 g/L and greater), the nucleation and growth of AgI on chrysotile was almost instantaneous and usually produced crystals up to 5 μm in diameter. At the lower concentrations, the growth was still extremely fast but with considerably smaller diameters resulting. All of the solutions with 1:1 ratios of KI and AgI tended to show some evidence for a background crystallization as well. However, chrysotile fibers could easily by identified (Figure 1).

Optimization of SNCG for Chrysotile

A number of concentration variations of the KI and AgI were used to determine an optimum concentration for the quantitative separation of chrysotile in environmental samples. Our goal was to slow the nucleation and growth slightly, reduce background crystallization, and still retain the apparent specificity

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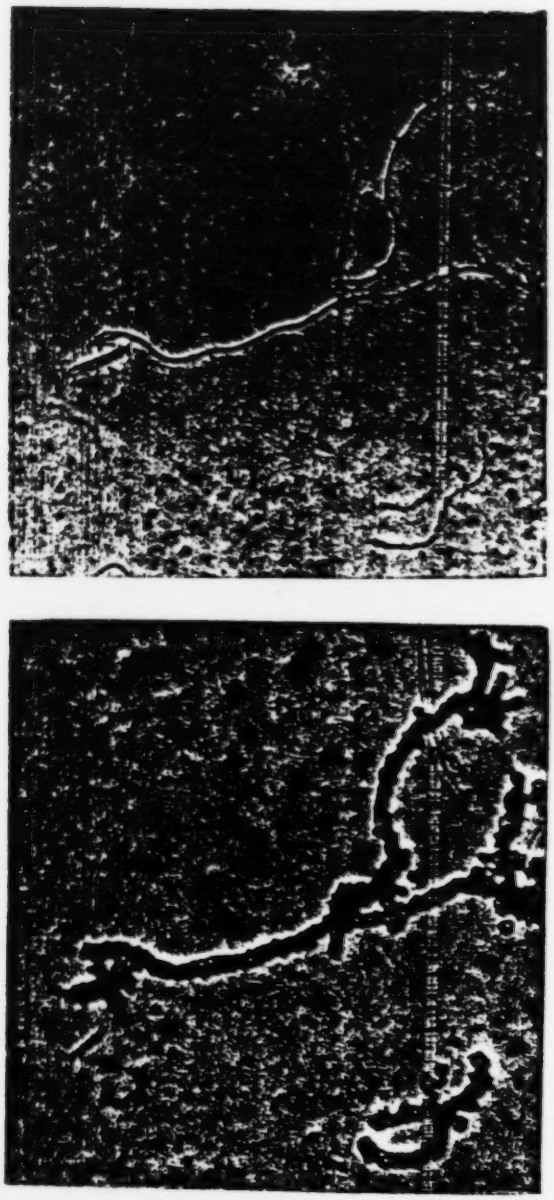

Figure 1. Chrysotile fibers before (top) and after overgrowth of silver iodide.

of the nucleation system. The results noted for crystal growth on chrysotile fibers (deposited on a glass slide) for several reagent concentrations are summarized in Table 1. In all cases, the initial solvent mixture was 1:1 ethylene glycol and acetone. The solution containing 20 g/L KI and 10 g/L AgI was selected as most appropriate for continuing studies and is identified as Reagent A. With this solution it was found that treating already decorated fibers with fresh reagent resulted in additional growth of the AgI crystals, suggesting the feasibility of using several treatments to obtain desired decorated particle size or density.

In subsequent studies investigating possible mineral interferences in the chrysotile SNCG system, it was discovered that relative humidity can play an important role. On days in which the relative humidity in the laboratory was less than 20 percent, the 20 g/L KI - 10 g/L AgI reagent was extremely stable in the supersaturated condition, so stable that chrysotile did not readily cause nucleation. After an evaluation of several concentrations, it was determined that a preparation at 15 g/L KI and 10 g/L AgI (identified as Reagent A2) appeared more suitable for use in continuing our study of SNCG.

The SNCG reagent solution described above is not compatible with water, with traces of moisture causing immediate overall crystallization of AgI. It was considered likely that the use of more KI and perhaps more acetone in the reagent solution would provide a longer period of metastability of the AgI supersaturation with water present. It was determined that some water could be added to solutions of 10 g/L AgI in 1:1 ethylene glycol and acetone containing 30 and 40 g/L KI. At the point where water caused crystallization, additional acetone produced clear solutions estimated as containing:

g/L		Ratio of Solvent Mixture				
KI	AgI	Glycol		Acetone		Water
20	5.0	0.4	:	1.0	:	0.25
20	6.7	0.7	:	1.0	:	0.4
28.5	7.1	0.8	:	1.0	:	0.5

All of the above solutions reacted instantaneously with chrysotile fibers; however, even in the absence of chrysotile, background crystals formed immediately when the reagent drops contacted a slide. The usefulness of Reagent A

TABLE 1. EFFECT OF CONCENTRATIONS ON AgI GROWTH

KI (g/L)	AgI (g/L)	Results
40	20	Slow initiation (30-60 sec), preferred sites apparent, ∿ 5 μm final diameter
40	10	Slow initiation, incomplete coverage on larger fibers, 9-10 μm where grown, low background
30	15	Slow initiation, incomplete coverage, 3-9 μm in diameter, low background
30	10	Slow initiation, incomplete coverage, 3-9 μm in diameter, low background
20	10	Rapid initiation (20-30 sec), very few blank spaces, 3-10 μm, low background
10	10	Very rapid initiation, complete coverage, high background, ∿ 5 μm growth
10	5	Very rapid initiation, complete coverage, ∿ 3 μm in diameter, high background
10	2.5	Very rapid initiation, complete coverage, ∿ 3 μm in diameter, high background

compositions for the SNCG decoration of environmental water samples is therefore complicated by the need to bring these samples to dryness and resuspend the solid matter in alcohol prior to reagent treatment.

In subsequent studies with Reagent A2, we noted the lack of good decoration of chrysotile fibers in our initial attempts to treat mixtures of quartz and chrysotile. Possible reasons for such behavior were considered to be the use of insufficient AgI solution, lack of uniform dispersion of the solids in the supersaturated solution, and perhaps an aging effect in which some crystals of AgI on the fibers grew at the expense of others. We therefore endeavored to improve the technique so as to negate the problems seen previously, especially to obtain good growth over the entire length of the chrysotile fibers.

For Reagent A, the final solvent composition was ethylene glycol. It was considered possible that because of the relatively high viscosity of the glycol, nucleation of AgI could occur at some sites on the chrysotile fibers and growth at those sites might well preclude the nucleation and growth at other sites, especially if the solution was not well stirred. In considering the primary function of the ethylene glycol, a nonsolvent for AgI in which supersaturation of AgI could be achieved, water came to mind as a less viscous substitute. Prior evidence indicated that some water was necessary to allow nucleation of the AgI. Total substitution of water for glycol was therefore attempted, with a greater ratio of KI to AgI to prevent spontaneous nucleation upon evporation of the acetone used in the unsaturated solution. An initial solution was prepared as follows:

Solvent: 50 mL acetone diluted to 100 mL with distilled water
4 g KI, dissolved readily in the above
0.5 g AgI, dissolved very slowly with agitation of the mixture.

A drop of a suspension of chrysotile in alcohol was allowed to dry on a slide and the area treated with 1 µL of the above mixture. Nucleation and growth were evident immediately, both on the fibers and in a very dense background. Dilution of the above reagent with acetone, up to an equal volume, still resulted in extremely rapid crystallization. Moreover, it was noted that at some time after the decoration had occurred, the AgI began to dissolve as the water evaporated. This was probably due to an increased concentration of KI in the remaining aqueous phase. (This suggests the use of aqueous KI solution

for eventually dissolving the AgI from decorated crystals after separation from extraneous materials.)

On the assumption that an intermediate mixture of water and ethylene glycol would provide a longer state of metastable supersatured AgI, another preparation was made in which an equal volume of 1:1 ethylene glycol:acetone was added to a portion of the above-mentioned solution in water-acetone. The final concentrations, then, were 20 g/L KI and 2.5 g/L AgI in 1:1:2 water: ethylene glycol:acetone. This solution was found to decorate chrysotile fibers well. It was noted, however, that crystal growth was rapid, occurring before all the acetone had evaporated. And with time, as the water evaporated, the AgI did dissolve. However, the decoration process at these concentrations was considered feasible for separation work in which evaporation of the aqueous phase would not occur.

A 40 mL sample of ethanol containing 220 µg chrysotile was evaporated to dryness, resuspended in a few mL of acetone and treated with 20 mL of the aqueous glycol-acetone solution. Evaporation of the acetone was accomplished by heat. The suspension was agitated periodically until crystallization was visually observed. A drop of suspension was observed microscopically and good decoration of the fibers was noted. On the basis of these evaluations, the 1:1:2 water to ethylene glycol to acetone solvent containing 20 g/L KI and 2.5 g/L AgI (identified as Reagent B) was used in most subsequent studies. This reagent, or modifications in composition thereof, was felt to be especially useful for samples containing water. For reference purposes, the compositions of the SNCG reagents for chrysotile employed in this program are given in Table 2.

Mineral Interference with SNCG Reagent for Chrysotile

Consideration has been given to mineral species that may result in a positive response to reagent treatment on the basis of morphological or structural similarity to chrysotile and coexistance with natural formations of chrysotile. A list of minerals considered and their response to reagent treatment is given in Table 3. For each case, mineral samples were ground with a mortar and pestle to pass a 200 mesh screen prior to reagent treatment. The lizardite sample showed a minor interaction, corresponding to crystals of AgI observed

TABLE 2

SNCG REAGENTS FOR CHRYSOTILE

Reagent	Solvent (Parts)			Additive Concentration (g/L)	
	Ethylene Glycol	Acetone	Water	KI	AgI
A	1	1	-	20	10
A2	1	1	-	15	10
B	1	2	1	20	1.5
B2	19	40	1	10	6.7

TABLE 3

MINERAL RESPONSE TO SNCG REAGENT FOR CHRYSOTILE

Mineral	Location	Source*	Reagent Response†	
			A	A2
Serpentines				
Chrysotile	Quebec	1	+	
Chrysotile	Rhodesia	1	+	
Chrysotile	Quebec	2	+	
Chrysotile	Quebec	3	+	
Antigorite	(R1385)	2	-	
Antigorite	-	4	-	(+)
Lizardite	-	4	(+)	+
Layered Silicates				
Muscovite		2	-	
Biotite	(R2429)	2	-	
Vermiculite		5	-	
Chlorite	California	3	-	
Kaolinite	New Mexico	3		-
Halloysite	Utah	3		-
Amphiboles				
Amosite	South Africa	1	-#	
Amosite	South Africa	2	+#	
Amosite	South Africa	3	-	
Anthophyllite	Finland	1	-	
Anthophyllite	(R1610)	2	-	
Crocidolite	South Africa	1	-	
Crocidolite	South Africa	3	-	
Actinolite	(R1841)	2	-	
Actinolite	(R1924)	2	-	
Actinolite	Vermont	3	-	
Tremolite	(R1596)	2	-	
Tremolite	Vermont	3	-	
Tremolite	Montana	3	-	
Hormblende	(R2816)	2	-	
Cummingtonite	(R2469)	2	-	
Cummingtonite	Minnesota	6	-	
Riebeckite	Colorado	3		-
Other Relicates				
Epidote	Colorado	3		-
Wollastonite	Mexico	3		-
Natrolite	Malaysia	7	-	

TABLE 3 (continued)

Mineral	Location	Source*	Reagent Response†	
Other Minerals			A	A2
Brucite	Quebec	3	-	-
Apatite	Quebec	3		-
Calcite	California	3		-

*1 UICC Asbestos samples
2 University of Minnesota
3 Wards
4 Harvard University
5 W.R. Grace Co.
6 Reserve Mining Co.
7 C. Thielen Collection

† + Complete decoration
(+) Partial decoration
- No reaction

A data sheet accompanying the University of Minnesota samples indicated that this sample was not chemically analyzed. Preliminary checks by electron beam probe analysis indicate that this mineral does not have the chemistry of amosite, revealing only the presence of Mg and Si. We suspect it is a sample of chrysotile that was mislabeled.

at widely spaced intervals on the surface of some larger plates of the mineral when treated with Reagent A. When retested with Reagent A2, the lizardite exhibited strong interaction, exhibiting nucleation and crystal growth of the AgI over its entire surface. The antigorite samples showed evidence of some nucleation and growth at isolated areas on its surfaces.

In summary, the only minerals reacting with the chrysotile reagent either strongly or partially were the closely related serpentine minerals lizardite and antigorite; the former is frequently contaminated with chrysotile. Transmission electron microscope photographs and selected area electron diffraction (SAED) patterns from individual particles of these minerals from Harvard University are given in Figures 2 and 3. Although the majority of the particles are platy, there is evidence for some elongated particles that correspond to fibers as defined by an aspect ratio of 3 to 1 or greater. The SAED patterns are distinctive. Some chrysotile fibers were observed in the lizardite sample which may account for the strong reagent interaction.

SNCG Reagent for Amphibole Asbestos

Several properties were considered for identifying candidate amphibole reagents, including lattice constant, surface charge, expansion coefficient, and atomic configuration at the surface. Due to the close crystallographic similarity of cummingtonite-grunerite (amosite), actinolite, crocidolite and tremolite, it is possible that a single reagent will be equally effective for all. Anthophyllite, being orthorhombic, would be expected to behave differently and require a different reagent. Lattice parameters for the monoclinic amphiboles are as follows[6]:

Mineral	a	b	c	β
Crocidolite	9.72-9.74	17.95	5.31	103.9°
Tremolite	9.74-9.84	17.8-18.05	5.26-5.28	104.7°-105.1°
Actinolite	9.86	18.11	5.34	105.0°
Amosite[7]	9.6	18.3	5.3	105.8°

Some candidate SNCG reagents were selected from compounds with similar parameters; namely,

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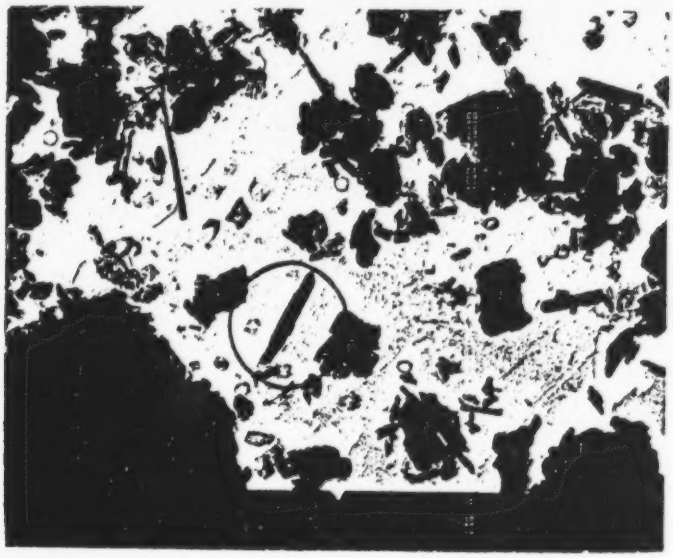

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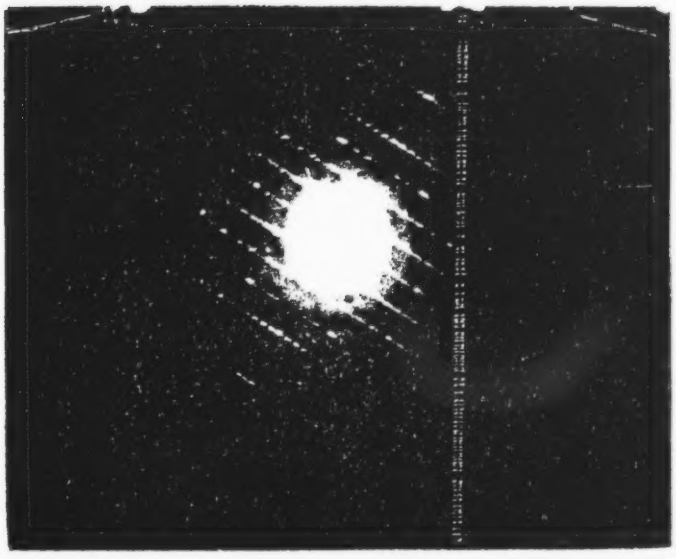
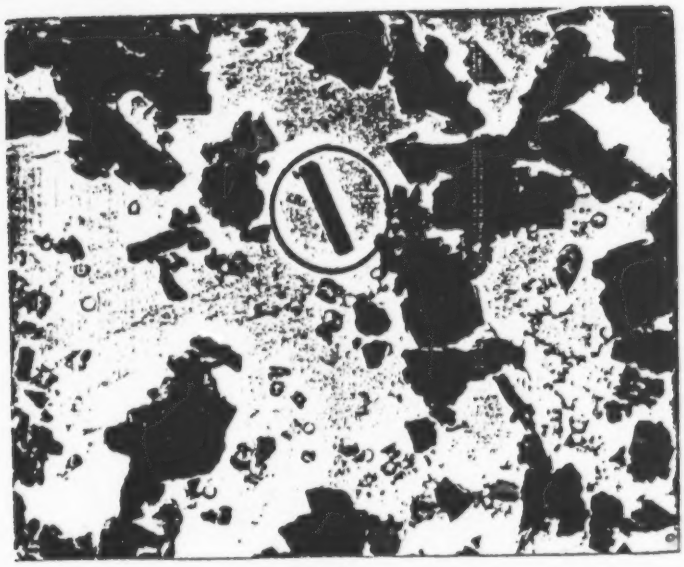
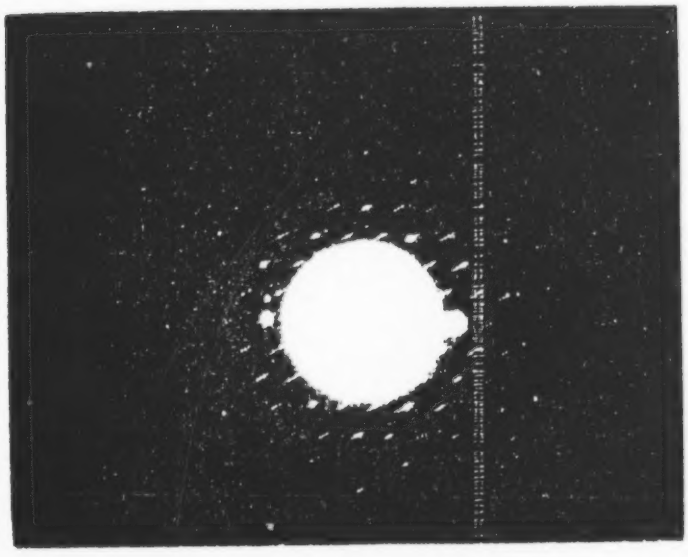


(b)

Figure 2. Transmission electron microscopy of lizardite (source 4). (a) Image, (b) Selected area electron diffraction [Circled particle in Figure 3(a)].



(a)



(b)

Figure 3. Transmission electron microscopy of antigorite (source 4). (a) Image, (b) Selected area electron diffraction [Circled particle in Figure 4(a)].

Lattice Parameters

Mineral	a	b	c	β
Uranyl oxalate trihydrate	9.41	17.04	5.61	98.2°
Copper dimethylglyoxime	9.73	17.05	7.4	107.1°
Potassium ferrocyanide trihydrate	9.34	16.87	9.34	90°

Uranyl oxalate has been synthesized and tested with crocidolite fibers dispersed on microscopic slides. Supersaturation has been achieved by: A) mixing solutions of uranyl acetate and oxalic acids in proper ratios and B) by allowing hot aqueous solutions of uranyl oxalate (solubility = ∿30 g/L) to cool to room temperature (solubility = ∿10 g/L). Some slight evidence of nucleation of crystal growth was seen from an approximately 16 g/L solution prepared at room temperature (Method A) and applied to crocidolite. A few widely separated areas on some fibers showed growth of short needles at about 90° to the long surface of the fibers. However, no indication of nucleation on crocidolite was observed when the supersatured solution prepared in hot water was used (Method B). Based on the observations using Method A, two additional oxalates (magnesium oxalate and lead oxalate) were tested, but with similar, nonspecific results. To produce supersatured solutions of the oxalates, soluble salts were mixed with solutions of oxalic acid. This was done in the presence of dry crocidolite fibers previously deposited on glass slides from a suspension in ethanol. The reagent components were placed as individual drops very close to each other and then brought into contact. The zone of mixing was observed microscopically. In all preparations, a few fibers showed some crystal growth; the background growth, however, was extremely dense.

In weakly ammoniacal solutions, copper dimethylglyoxime has been reported to form as green crystals that dissolve in excess ammonium hydroxide. An experiment was conducted to see whether such crystals would form on crocidolite fibers, the reagent solution being prepared from solutions of dimethylglyoxime in alcohol and copper acetate in water to which ammonium hydroxide was added. The reagent solution was deep red and red crystals formed spontaneously as the excess NH_4OH evaporated, as would occur for homogeneous nucleation. There was no evidence for preferential nucleation on the crocidolite, however. Potassium ferrocyanide trihydrate, the remaining of the three compounds with close lattice parameters to amphiboles, was also tested and found not to be nucleated by crocidolite.

A number of readily vaporizable compounds were also tested as potential reagents for crocidolite. In addition to their ease of sublimation, they represented a variety of chemically active materials and consisted of iodine, dimethylglyoxime, urea, and oxalic acid. While none of these were observed (microscopically) to preferentially nucleate and grow on crocidolite fibers, oxalic acid exhibited a definite pattern of avoiding such fibers when condensing on the microscope slide. While the exact reason for this is unknown, it suggests that compounds with basic functions, e.g., amino groups, should be examined. As a result, both 1,6-diaminohexane and 1,6-dihydroxyhexane were tested in vapor form. Both compounds were observed to condense in liquid form on the crocidolite fibers as well as on the glass slide background. Further work with these compounds was limited to the diol form since the diamine form was very unstable in air. The diol form was then tested in the form of supersaturated solutions in water and alcohol, but with no evidence of preferential nucleation by the crocidolite fiber. It was also tested in the form of a supercooled melt; the crocidolite did not serve as a nucleation site.

In addition to the above, sodium metasilicate was screened as a potential SNCG reagent on deposits of both crocidolite and amosite (UICC). The silicate was applied in aqueous solutions and observed microscopically as crystallization occurred during evaporation. Neither of the amphiboles acted as nucleation sites for this compound.

Benzanthrone was also tested, in vapor form, on the amosite asbestos. Condensation, in a supercooled liquid state, was observed both on the fibers and throughout the background of the glass slide.

In summary, although some reagents were found to crystallize on amphibole fibers, the background growth was extremely dense. No reagents were found that were satisfactorily selective to amphibole asbestos.

STANDARD SAMPLES

In the studies leading to the development of the special x-ray diffraction procedure for measuring small masses of chrysotile, Fatemi et al[3] carried out a series of experiments to determine the effect of ultrasonication (to disperse fibers after low temperature ashing) on x-ray diffraction intensity. It was found that long sonication time leads to a decrease in x-ray intensity due to

a reduction in fiber size and fiber losses. For the present program, it is also necessary to establish that the ultrasonic agitation process does not degrade the fiber surface, preventing selective nucleation of crystal growth.

Consequently, several processing conditions have been applied to UICC Canadian chrysotile to determine conditions for breaking up fiber bundles and suitability for preparing a standard suspension. Conditions are as follows:

No.	Liquid	Concentration	Preparation Procedure
S1	Ethanol	4.4 mg/L	Add 2.6 mg asbestos to 600 ml ethanol, agitate with US horn (medium setting) for 5 minutes, periodically hand shake for ∿4 weeks.
S2	H_2O	4.6 mg/L	Add 1.4 mg asbestos to 300 ml H_2O, agitate, etc...as above.
S3	Ethanol	11 mg/L	Add ∿1 mg asbestos to 2 ml ethanol in 5 ml beaker; agitate with US horn (low setting) for 50 minutes, make up to 100 ml.
S4	H_2O*	100 mg/L	Add ∿0.6 mg asbestos to 2 ml H_2O* in 15 ml tapered test tube, agitate with US horn (low setting) for 50 minutes, make up to 6 ml.
S5	H_2O*	∿110 mg/L	Hand grind asbestos under acetone, dry, transfer to 15 ml tapered test tube, add 6 ml H_2O*, agitate in US bath for 10 minutes, centrifuge at 200 g's for 3 minutes and recover supernate.

Most of the samples were examined subsequently by scanning electron microscopy, with the following results:

S1 - fiber bundles are largely broken down; typical fiber dimensions are diameter: 0.1 to 0.3 μm, fiber length: 10 to 50 μm.

S2 - not examined. Optical microscope examination reveals numerous fiber bundles, indicating little size reduction.

*Water contains 1% aerosol OT as a wetting agent.

S3 - fiber bundles are mostly broken down; fibers tend to clump, which may be due to the nature of drop drying; typical dimensions are slightly smaller than for S1 above.

S4 - there is a substantial reduction in fiber bundle size. Discrete bundles having diameters of 1-2 μm remain. Typical fiber dimensions are diameter: 0.2-0.5 μm, length: 50-100 μm.

S5 - No fibers are present. For conditions employed, particles with an aerodynamic diameter >0.5 μm would have settled out. The conclusion is that fiber bundles did not break down by this treatment.

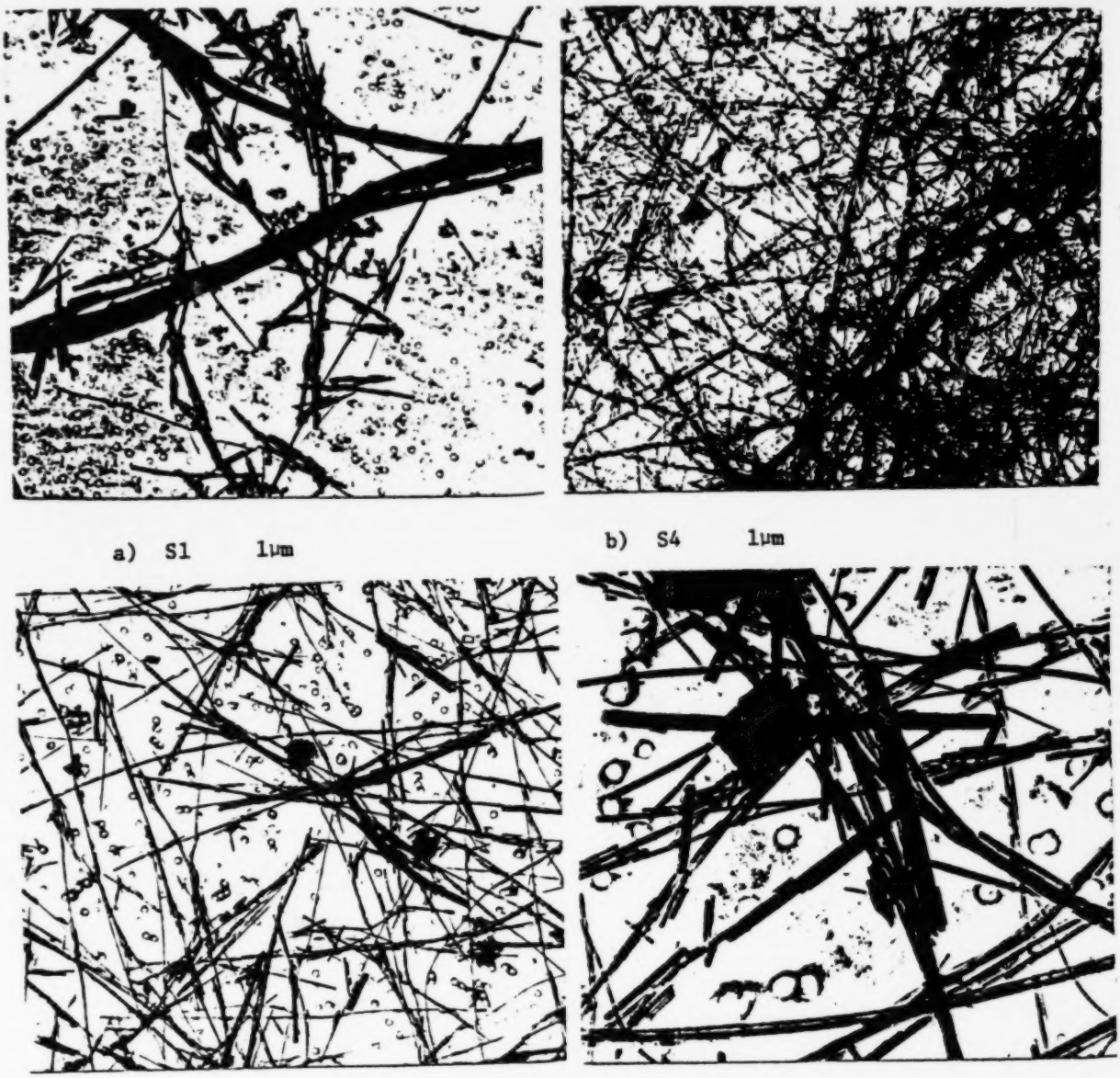
On the basis of the above observations, S1 and S3 and possibly S4 appear to yield useful suspensions of chrysotile.

Samples of these were prepared for transmission electron microscope (TEM) examination by filtering an aliquot through 0.1 μm pore size Nuclepore, carbon coating and Jaffe wick solvent extraction. Representative photographs are given in Figure 4.

Samples S1 and S4 are observed to contain numerous fiber bundles having diameters of 0.2-0.3 μm as well as many fibers of smaller diameter. A loading of 50 $\mu g/cm^2$ is appropriate for general viewing but a lower concentration would be required for fiber counts or measurements. Sample S3 shows good breakdown and dispersion of fibers and represents the best suspension preparation procedure. The presence of individual fibrils can be seen at higher magnification.

During the course of the program additional standard suspensions of chrysotile and quartz were required to prepare mixed mineral samples of known composition; these standard suspensions, identified as S6 and S7, respectively, were prepared by the procedure used for S3 as described above. A summary of the various mineral standard suspensions prepared in the program is given in Table 4.

Various mineral samples were prepared during the program to quantitatively evaluate various processing steps, including preseparation and recovery after reagent treatment and separation. These consisted mostly of mixtures of UICC Canadian chrysotile and quartz as well as a sample of crushed stone from the Rockville, MD quarry. The latter sample, collected on April 6, 1977, was



a) S1 1µm

b) S4 1µm

c) S3 1µm

d) S3 0.5µm

Figure 4. Transmission electron microscope photographs of UICC Canadian chrysotile suspensions: a) S1-66 µg/cm^2, b) S4-006 µg/cm^2, c) and d) S3-69 µg/cm^2.

TABLE 4. COMPOSITION OF STANDARD SUSPENSIONS

No.	Mineral		Liquid		Concentration
	Type	Amount	Type	Amount	
S1	UICC Chrysotile (Canadian)	2.6 mg	Ethanol	600 ml	4.4 mg/L
S2	UICC Chrysotile (Canadian)	1.4	Water	300	4.6
S3	UICC Chrysotile (Canadian)	1.0	Ethanol	100	11
S4	UICC Chrysotile (Canadian)	0.6	Water	6	100
S5	UICC Chrysotile (Canadian)		Water	6	~110
S6	UICC Chrysotile (Canadian)	5.0	Ethanol	500	10
S7*	Quartz	10	Ethanol	200	50

*A drop of this suspension was placed on a glass slide and 100 particles were counted at 400X. All but one were 5 μm in diameter or smaller, the one being about 12 μm in diameter

supplied by Jack Wagman, EPA Project Officer. For use, a single stone was pulverized in a diamond mill until all particles passed a 325 mesh given.

Samples for evaluation were prepared by adding ethanol or acetone to weighed powders and then following the procedure described for sample S3 above, by adding aliquots of the standard suspensions given in Table 4 followed by hand shaking, or by weighing an aliquot of a standard suspension to weighed powders followed by ultrasonic agitation with a horn for 5 to 10 minutes.

PRESEPARATION EXPERIMENTS

Environmental air samples collected on a membrane filter may contain considerable amounts of organic matter that can interfere with the electrostatic alignment procedure for chrysotile fibers that has been developed by the Naval Research Laboratory[2]. This organic matter can be removed through combustion, which typically is carried out by means of oxygen plasma ashing (sometimes referred to as low temperature ashing, LTA). Preliminary studies of LTA conducted by the NRL indicated the need for very careful control of conditions to achieve successful results. The ashed material is resuspended in an appropriate liquid and dispersed by ultrasonic agitation with a horn. In addition to dispersing the ash, the ultrasonic energy of the horn tends to defibrilate clumps of chrysotile asbestos fibers, providing a more uniform sample. This suspension can be refiltered through a suitable membrane filter, such as polycarbonate, for preparing transmission electron microscopy samples for fiber counting or can be used directly for electrostatic alignment of the contained fibers by the NRL device.

To evaluate the preseparation process, including the ability to quantitatively recover asbestos fibers, suspensions of chrysotile and quartz were filtered through membrane filters (polycarbonate and mixed cellulose esters) which were then ashed in a low pressure oxygen plasma, resuspended in alcohol, ultrasonically agitated to break up the ash and refiltered through a silver membrane filter. These filters, together with single phase calibration standards similarly filtered directly from the original stock solutions, were analyzed for mineral content by x-ray diffraction, using the intensity of the (101) quartz and (002) chrysotile diffraction peaks.

The following effects and levels were considered:

Effect	Level 1	Level 2
Membrane Filter	0.1 μm Nuclepore (NF)	0.22 μm Millipore (MF)
Mineral Concentration	50 μg Chrysotile + 1 mg Quartz	200 μg Chrysotile + 1 mg Quartz

Six samples each were prepared from 5 ml and 20 ml (Level 1) or 20 ml each (Level 2) of standard suspensions S6 and S7, respectively. Calibration samples included 10, 25, 50, 75 and 100 ml samples of S2 filtered through 25 mm diameter 0.8 μm silver membrane filters and 5, 10, 25 and 50 ml of S6 and 20 and 40 ml of S7 filtered through 25 mm diameter 0.45 μm silver membrane filters. Ashing was carried out in a Plasmod system with an oxygen flow of 80 cm^3 per minute and a pressure of 0.2 torr. The 47 mm diameter membrane filters were folded several times and placed in 8 mm inside diameter by 25 mm long test tubes. The tubes were supported in beakers for ashing. The samples were initially ashed at a low power setting (abou. 15 watts) for a minimum of four hours (preferably over night) followed by four hours at 50 watts. After ashing, water was added to a level of 20 mm and the samples were agitated in an ultrasonic bath for 30 minutes. The contents were then washed into 50 ml beakers which were filled to about 40 ml. These suspensions were then filtered through 25 mm diameter silver membrane filters.

All filters were examined for chrysotile and silica content by x-ray diffraction, using 60 second counts of the (002) and (101) peaks, respectively, and Cu K_α radiation at 40 KeV and 20 ma. X-ray diffraction calibration data are given in Figure 5. No difference is observed relative to the silver membrane filter pore size (0.45 vs 0.8 μm) or for the chrysotile syspension (S2 - 4.6 μg/ml). The silica data are in agreement to values obtained in other studies concerning the analysis of respirable silica dust.

Sample recoveries after ashing are presented in Table 5. The data suggest considerable sample loss during the ashing process, corresponding to 15 to 30 percent recoveries at the 50 μg chrysotile level, 35 percent at the 200 μg level, and 60 percent for silica at 1000 μg. The Nuclepore filter tends to give somewhat lower recoveries in all cases.

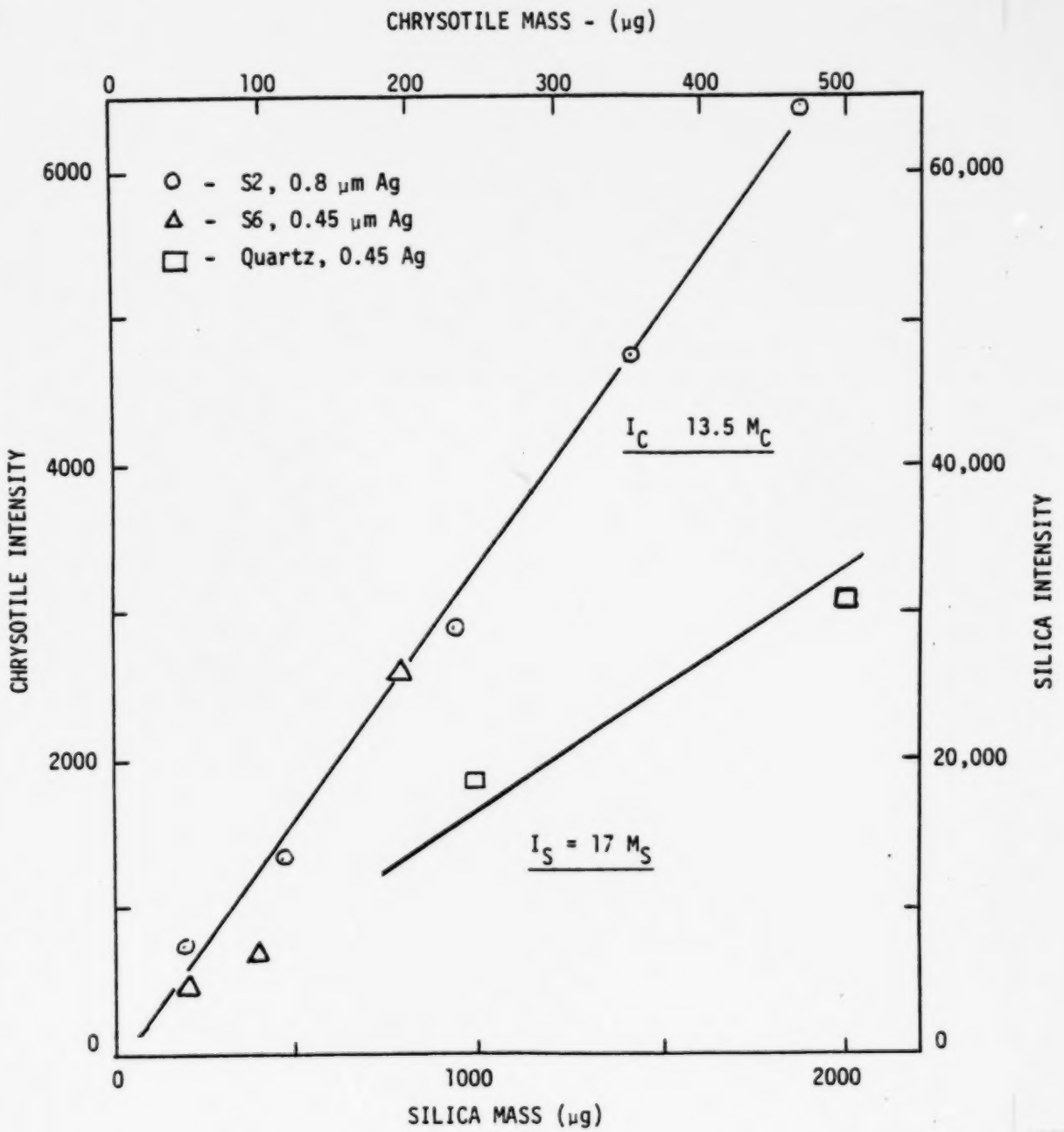


Figure 5. X-ray diffraction calibration data.

TABLE 5. CHRYSOTILE PLUS QUARTZ RECOVERIES AFTER LOW-TEMPERATURE ASHING BY X-RAY DIFFRACTION ANALYSIS

	5 ml C/5 ml S				20 ml C/5 ml S			
	MF		NF		MF		NF	
	C	Q	C	Q	C	Q	C	Q
	Mass (µg)							
Suspension	50	1000	50	1000	200	1000	200	1000
Run 1	13	539	18	479	50	453	35	321
Run 2	11	515	2	848	91	520	68	743
Run 3	17	714	1	628	91	851	90	798
	Percent Recovery							
Run 1	26	54	36	48	25	45	18	32
Run 2	22	52	4	85	45	52	34	74
Run 3	34	71	2	63	45	85	45	80
Average	27	59	14	65	38	61	32	62

In light of our general experience with mass recoveries after low-temperature ashing, which are typically in the range of 80 to 100 percent for respirable dust samples, it is difficult to explain the low recoveries observed for these experiments. Mineral particle agglomeration as a result of ashing may result in a different orientation relationship of the particles compared to the standards, thus influencing the x-ray results. Based on a review of these data, the EPA Project Officer recommended using x-ray fluorescence analysis of Mg and Si as an independent measurement procedure for chrysotile and silica contents. This measurement procedure would not be affected by particle agglomeration (from the ashing step) or particle orientation, both of which could influence x-ray diffraction measurements.

Consequently, the various calibration standards and ashed samples previously analyzed by x-ray diffraction were reanalyzed by x-ray fluorescence. From pure chrysotile standards (Figure 6) it was determined that

$$I_{Si}\ (C) = 475 + 14.6\ M_C$$

$$I_{Mg}\ (C) = 4.59\ M_C$$

and

$$I_{Si}\ (C) = 475 + 3.18\ I_{Mg}$$

It was necessary to take into account the distribution of silicon between quartz and chrysotile. Therefore, replicate quartz plus chrysotile standards were prepared and the following results were obtained:

	I_{Si}	I_{Si} (corrected)
1000 g Q + 50 g C	24080	23346
	22159	21525
1000 g Q + 200 g C	26285	25174
	22114	21003

Average - 22762

Coefficient of Variation (%) - 8.3

From the above, sample recoveries are determined by the expressions

$$M_C = 0.218\ I_{Mg}$$

$$M_Q = 0.0439\ [I_{Si} - (475 + 3.18\ I_{Mg})]$$

The results for triplicate sets of four samples each are given in Table 6.

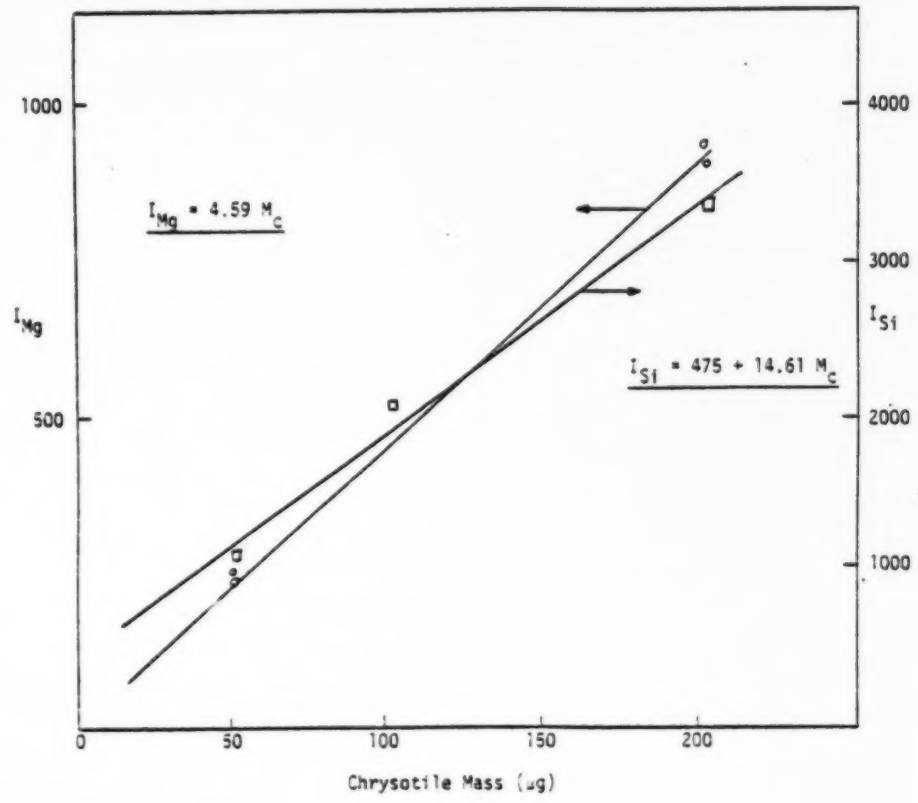


Figure 6. X-ray fluorescence calibration data for chrysotile.

TABLE 6. CHRYSOTILE PLUS QUARTZ RECOVERIES AFTER LOW-TEMPERATURE ASHING BY X-RAY FLUORESCENCE ANALYSIS

	5 ml C/5 ml S				20 ml C/5 ml S			
	MF		NF		MF		NF	
	C	Q	C	Q	C	Q	C	Q
	Mass (µg)							
Original Suspension	50	1000	50	1000	200	1000	200	1000
Run 1	36	608	33	640	115	668	48	967
Run 2	48	967	46	704	155	896	138	802
Run 3	50	807	37	759	179	974	160	919
	Percent Recovery							
Run 1	72	61	66	64	58	67	24	97
Run 2	96	97	92	70	78	90	69	80
Run 3	100	81	74	76	90	97	80	92
Average	89	80	77	70	75	85	58	90
Average (Run 2 and Run 3)	98	89	83	73	84	94	75	86

Recoveries are substantially higher than values measured by x-ray diffraction. It is possible that the ash was not completely dispersed, leading to a nonuniform distribution of particles. Also, signal strength (counts per second) was much higher for x-ray fluorescence, with less scatter in the data. Recoveries for Run 1 were 60 to 70 percent for most samples. Runs 2 and 3, which were ashed at the same time, provided substantially higher recoveries ranging from 75 to 100 percent. The results with Millipore filters indicate recoveries about 10 percent greater than for Nuclepore filters. The observed levels of recovery are consistent with past experience in low-temperature ashing losses and are considered to be adequate for the program requirements.

REAGENT TREATMENT AND SEPARATION EXPERIMENTS

Over the course of study several approaches have been evaluated to selectively separate AgI decorated chrysotile from other coexisting particulate matter. In terms of program objectives, it was considered more important to obtain good asbestos recoveries after separation than to completely avoid carryover of extraneous matter, as any increase in asbestos concentration within the separated matter would be expected to benefit the fiber alignment process used for preparing x-ray specimens. The following sections emphasize the good asbestos recovery approach to separation.

High Density Liquid

Initial experiments were carried out with small volumes ($\sim$1 ml) of mineral samples M1 and M2. After reagent decoration, about 1 ml of bromoform was added to the test tube. As bromoform has a density of 2.8 mg/cm^2, the heavy AgI decorated particles, with a density of 5.5-5.7, were expected to sink to the bottom of the test tube when the lighter quartz particles (density of 2.65 g/cm^3) would remain suspended in the bromoform or would perhaps rise and float. The experiments with bromoform were unsuccessful. With the direct addition of bromoform to the suspension in glycol, the materials tend to remain at the interface of the liquids. Removal of the glycol, by addition of water or alcohol followed by removal of the supernate, results in the solids migrating to the tube walls. In addition, inspection of material removed from the bromoform layer shows that some chrysotile fibers do not have any AgI overgrowth. The cause for this condition is not known.

At a later point in the program, separation experiments were performed with methylene iodide, having a density of 3.3 g/cm^3, using mixtures of 66 µg chryostile - 1000 µg silica. Qualitatively, the material that floats (i.e., the low density material) tends to adhere to the test tube at the meniscus, making removal difficult. This material reentrains in the liquid column very easily (i.e., table vibration), suggesting the presence of forces other than gravitational.

As a result of the problems encountered, the heavy density liquid approach was temporarily put aside in favor of Stokes settling.

Stokes Settling

Mixtures of chrysotile and quartz (M3, M6 and M7) were treated with the AgI reagent followed by separation of AgI-chrysotile and SiO_2 fractions by Stokes settling. Separation was carried out in a test tube by filling to a height of 8 cm, agitating and allowing to settle for one-half hour. The calculated settling rates for the decorated chrysotile (assumed to be 5 µm diameter spheres of AgI) were:

	AgI & Chrysotile	SiO_2
Original Solution	10 min.	30 min.
Water	6 min.	18 min.

The procedure was as follows: after initial settling, the tube was inverted and allowed to settle for 10 minutes, after which the upper 4 cm supernate was withdrawn and placed in a separate container. By design, all of the silica should be in the withdrawn supernate and the decorated chrysotile retained. After refilling to the 8 cm mark, the process was repeated three (M3) or four (M6) times, allowing a six minute settling time for the water. After separation, the sample was treated with hypo to dissolve the AgI. An aliquot corresponding to 1/100 of the original sample and 1/250 of M7 (untreated suspension) was filtered through a 47 mm diameter, 0.1 µm pore size Nuclepore filter which was carbon coated and processed for TEM and SEM analysis. The remaining sample volume was filtered through a 25 mm silver membrane filter (1.2 µm pore size) for x-ray diffraction.

The sample quantities were as follows:

No.	Original (mg)			TEM and SEM* (μg/cm²)		X-ray* (mg/cm²)	
	C	S	%C	C	S	C	S
M3	3.2	5.2	38	2.5	4.1	1.5	2.4
M6	4.4	7.5	37	3.4	5.8	2.1	3.5
M7	8.9	14.8	38	2.7	4.2	4.2	6.9

*Assumes all S (silica) was collected in the supernate and all C (chrysotile) was retained in the settled sample.

Scanning electron micrographs of an original (M7) and separated (settled-M3A and supernate-M3B) samples are given in Figures 7 and 8, respectively. The suggestion of an increased concentration of chrysotile is observed in the M3A sample (Figure 8) compared to the starting sample (M7, Figure 7) or supernate (M3B, Figure 8). However, the photographs shown are subjective with respect to the area exhibited. As with the TEM samples, it is possible to find fields that support good separation and other fields that lead to the opposite conclusion. Therefore, x-ray diffraction was employed as a means of comparing the effectiveness of separation. As a very rough estimate of relative amounts of phases within the various samples, data were collected on the basis of average peak intensity for the two most intense peaks of silica and chrysotile. The results are as follows:

No.	Intensity			Amounts Recovered (%)*			
	C	S	Ratio	C	S		
M7	76.0	360.0	0.21	100	100		
M3A	42.0	96.0	0.44	110	77		
M3B	4.0	30.5	0.13	15	24	125	101
M6A	82.0	200.0	0.41	216	109		
M6B	4.5	85.0	0.05	12	46	228	155

*Using M7 results as a calibration factor.

From the intensity ratio it is observed that the separated fractions are more concentrated in chrysotile (as compared to silica) by about two times. The supernate samples contain less chrysotile than in the original sample, but separation is only partial (roughly a two-times enchancement in chrysotile

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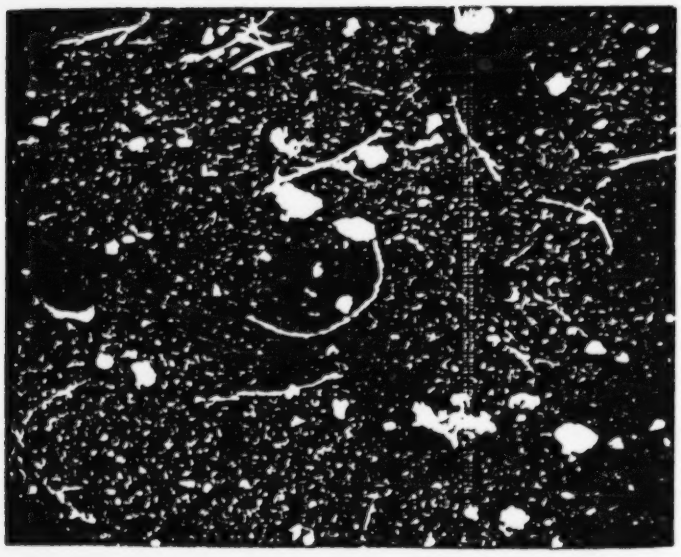
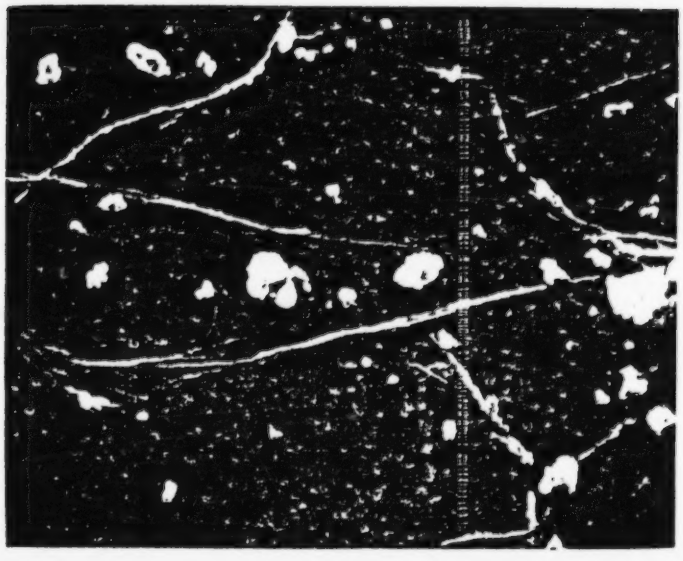
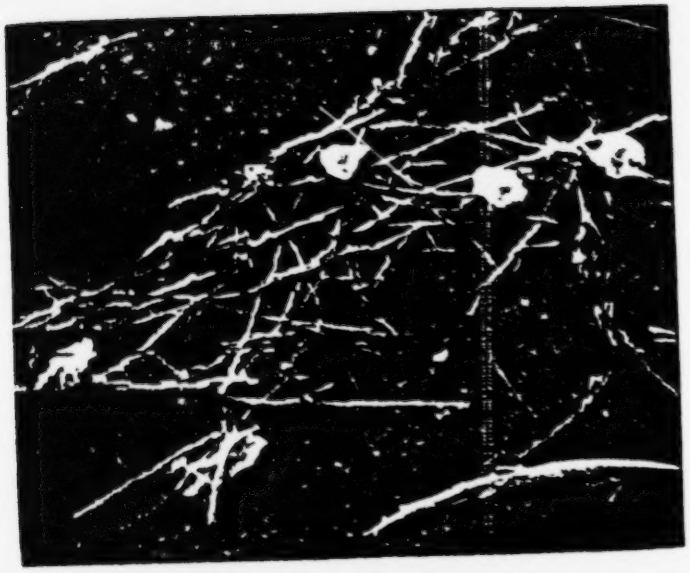


(a)

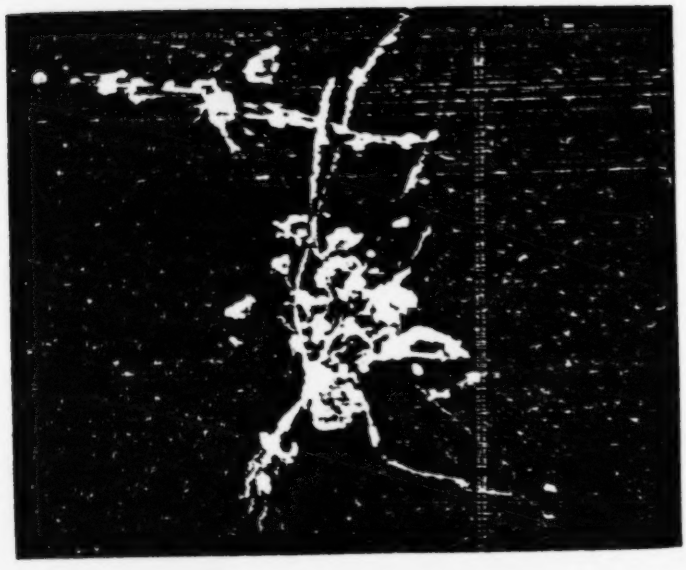


(b)

Figure 7. Scanning electron microscope photographs of chrysotile and silica mixture M7 - total mass of 7.9 µg/cm^2 (a) 2200X, (b) 5200X.



(a)



(b)

Figure 8. Scanning electron microscopy photographs of chrysotile and silica mixture M3 at 5200X.
(a) Separated sample (M3A), (b) Supernate Sample (M3B).

content in the separated sample). In terms of amounts recovered, roughly 90-95 percent of the chrysotile is present in the separated sample, which also contains 70-75 percent of the quartz.

The conclusion of this work is that quartz is not completely separated, probably due to the presence of several particles larger than 5 μm diameter (contributing to a major portion of the mass) which settled out rather than being separated with the supernate. In addition, a portion of the chrysotile (about 10%) was not separated.

Subsequently, optical microscopic examination of an AgI-treated mixture showed that the crystal growth occurred only at a few sites on some fibers, and where it occurred, the AgI crystals grew to diameters on the order of 30-40 μm. Presently, we attribute such behavior to either a poor distribution of the fibers in the supersaturated reagent and/or subsequent aging (ripening) of crystals at selected sites on the fibers.

Based on the above observations, calculations of the theoretical coverage of chrysotile fibers by evenly distributed reagent has shown that the amount of AgI in solution for these experiments was not sufficient for the expected growth. We have derived the following expressions for theoretically describing a uniform coverage and density of the final decorated product:

$$V_{AgI}/V_C = \left(\frac{d_T}{d_C}\right)^2 - 1$$

$$M_{AgI}/M_C = 2.268\ V_{AgI}/V_C$$

$$D_T = \frac{M_{AgI} + M_C}{V_{AgI} + V_C}$$

where

d_T = final diameter of fiber plus overgrowth

d_C = diameter of chrysotile fibers

V_{AgI} = volume of overgrowth

V_C = volume of chrysotile fibers

M_{AgI} = weight of AgI in overgrowth

M_C = weight of chrysotile fibers

D_T = density of fibers and overgrowth

Values for D_T and the ratios V_{AgI}/V_C and M_{AgI}/M_C are as follows:

$\frac{d_T}{d_C}$	D_T (g/cm^3)	$\frac{M_{AgI}}{M_C}$	$\frac{V_{AgI}}{V_C}$
100	5.67	22678	9999
50	5.67	5668	2499
25	5.67	1415	624
10	5.65	225	99
5	5.5	54.4	24
2	4.9	5.8	3
1.4	4.2	2.2	0.96
1.1	3.1	0.48	0.21

From the above data the density of the decorated chrysotile fiber approaches that of AgI at a tenfold ratio of final diameter to chrysotile diameter and a mass ratio of 225 AgI to 1 of chrysotile. In our experiments, we treated 3.2 and 4.4 mg quantities of chrysotile (in the mineral mixtures) with only 20 mg AgI each, resulting in mass ratios of 6.25 and 4.55, which give final densities (D_T) of 4.8 g/cm^3 and 4.5 g/cm^3. Such densities should have resulted in better separations than indicated by the x-ray and electron microscope examinations if the AgI had been properly distributed.

Based on the considerations presented above, a second set of experiments was carried out using mineral samples M8 through M12. More effective mixing of the suspension during nucleation and growth was attempted by using lesser amounts of total solids (~1 mg/sample) and larger volumes of reagent solutions. Also, the quartz was presized to less than 5 μm in diameter (by Stokes settling) to prevent quartz "heavies" from settling out with the AgI decorated chrysotile. The composition of the four mixtures was as follows:

M8	2.7% chrysotile	0.001684g silica
M9	5.6% chrysotile	0.001595g silica
M10	10.6% chrysotile	0.000994g silica
M11	22.7% chrysotile	0.00082g silica

These, together with a pure chrysotile sample (M12) were treated with the SNCG reagent. To reduce reagent volume the salt concentration was doubled, corresponding to 40 g/L KI and 5 g/L AgI in 1:1:2 water:ethylene glycol: acetone. After treatment, the heavy particles were separated by 4-stage Stokes settling.

The settled and supernate fractions were filtered through 25 mm diameter silver membrane filters and were analyzed by x-ray diffraction for chrysotile content, using the calibration curve given in Figure 7. The experimental results are presented in Table 7.

The results are disappointing in that they indicate poor recoveries of the separated chrysotile (20-30 percent) and only about half of the chrysotile sample accounted for. In comparison, 40-60 percent of the quartz is carried along with the separation with only 20-30 percent found in the supernate, accounting for a recovery of 70-75 percent. In essence, there is no concentration of the chrysotile with respect to quartz, with up to 50 percent of the chrysotile lost within the system. Microscopic examination of these samples indicated a good, uniform deposit of the SNCG reagent on the chrysotile. The poor recoveries and lack of concentration cannot be explained. It is speculated that the Stokes settling was ineffective in that fine particles were carried along with large particles due to impingement or other attractive forces. The presence of chrysotile in the supernate is less easily reconciled. Possible explanations are attraction and adherence to the walls of the test tube or incomplete decoration due either to consumption of the reagent by the growth of already decorated fibers rather than nucleation on new fibers or alternatively, the presence of inactive sites or fibers with respect to decoration. A few drops of supernate from a similarly prepared sample were examined by optical microscopy and the chrysotile fibers exhibited normal levels of decoration. It is concluded that particle interactions occur which impede the settling out of the decorated fibers.

High Density Liquid and Centrifugation

Based upon the disappointing results of the separation experiments described above, a review meeting was held with the EPA Project Officer. He suggested centrifugation in a heavy liquid as a means of increasing the forces

TABLE 7. ANALYSIS OF MINERAL MIXTURES BY X-RAY DIFFRACTION

SAMPLE NO.	ORIGINAL AMOUNT (µg)	
	CHRYSOTILE	QUARTZ
M8	47	1680
M9	95	1600
M10	118	990
M11	236	800
M12	220	-

	AMOUNT CHRYSOTILE RECOVERED (%)		
	SEPARATED	SUPERNATE	TOTAL
M8	23	30	53
M9	21	12	33
M10	28	90	118
M11	31	20	51
M12	65	79	144

	AMOUNT QUARTZ RECOVERED (%)		
	SEPARATED	SUPERNATE	TOTAL
M8	34	31	65
M9	44	32	76
M10	59	17	76
M11	41	28	69
M12	-	-	-

acting on the particles (and suspension liquid), enhancing the opportunity for separation. This approach was evaluated in a final set of samples intended to represent environmental samples, including airborne matter and rock. For this purpose, appropriate quantities of suspensions S6 (10 µg chrysotile/ml) and S7 (200 µg quartz ml) were used to prepare samples of the following:

M13 100 µg chrysotile
M14 100 µg chrysotile + 500 g quartz

Duplicates (identified as A and B) of each of the above mineral samples were filtered through 47 mm-0.8 µm pore size Millipore filters followed by low-temperature ashing by the procedure described above. Also, a sample of serpentine rock (Rockville, MD crushed stone sample E, purported to contain 1.8 percent chrysotile) was milled in a diamond mill to pass a 325 mesh screen. This material was identified as M15. Weighed amounts of the dry powders, corresponding to 1.1 mg in A and 1.0 mg in B, were introduced directly into SNCG reaction tubes after which a small amount of acetone (~2 ml) was added.

The contents of the M13 and M14 pairs were transferred from the short tubes (28 mm long by 7.5 mm I.D.) used for low-temperature ashing to longer reaction tubes (75 mm length) of the same I.D. Acetone was used to rinse all particulates from the short tubes to the longer ones. The three sets of samples were agitated with an ultrasonic horn to disperse the minerals and the filter residue. For these experiments the SNCG reagent composition was 6.67 g/L AgI and 10.0 g/L KI in a 1:19:40 mixture (by volume) of water: ethylene glycol:acetone. Initially, 2 ml of the SNCG reagent were added and the acetone allowed to evaporate at ambient conditions. Stirring was done with the use of sealed capillary tubes. Following the evaporation of the acetone, a second 2 ml volume of SNCG reagent was added and the acetone again allowed to evaporate. The mixtures were then centrifuged until the upper layer was clear. That layer, consisting primarily of the KI solution, excess AgI, and ethylene glycol was removed by pipette. The residue was then rinsed with about 3 ml of ethanol, centrifuged, and the alcohol removed by pipette. This rinse treatment was done four times followed by a final rinse with acetone. The combined supernates (ethylene glycol, alcohol and acetone) was labeled F1.

The air-dried solids were next treated with 1 ml methylene chloride and dispersed ultrasonically. Centrifugation (20,000 g) was then used to aid in separation of the AgI-coated material from any less dense material present. The supernate was drawn off by pipette and the residue rinsed with small amounts of acetone. The supernate and rinses were combined and labeled F2.

The residual solids were than treated with aqueous KI (62.5 g/l) to dissolve the AgI and leave the chrysotile fibers in the undecorated state for filtration on silver membranes for analysis by x-ray fluorescence. This fraction was identified as F3.

Each of these fractions was filtered through a 25 mm diameter, 0.45 μm silver membrane filter after which x-ray fluorescence analysis of Si and Mg peak intensity for each sample was carried out with a Philips vacuum spectrometer using a chromium target at 45 KV and 25 ma and using a gypsum analyzing crystal, proportional detector and pulse height analyzer. With more stringent conditions for pulse height selection than used previously (i.e., Figure 6), the calibration standards consisting of pure chrysotile and chrysotile + quartz suspensions gave the following:

$$I_{Mg}\,(C) = 1.54\,M_C \qquad (1)$$

$$I_{Si}\,(C) - 6.21\,M_C \qquad (2)$$

From the quartz plus chrysotile samples it was found that

$$I_{Si}\,(Q) = 8.163\,(M_Q) \qquad (3)$$

and, from Eqs. 1, 2 and 3

$$M_Q = 0.1225\,I_{Si} - 0.494\,I_{Mg} \qquad (4)$$

$$M_C = 0.649\,I_{Mg}$$

Data for the unknown samples were corrected for background and mineral phase masses were determined by Ews. 4 and 5. The results are given in Table 8.

TABLE 8. DISTRIBUTION OF MINERAL COMPONENTS AND RECOVERIES FROM EVALUATION SAMPLES

	13A		13B		14A		14B		15A		15B	
	C	Q	C	Q	C	Q	C	Q	C	Q	C	Q
Starting Amount (µg)	100	-	100	-	100	500	100	500	-	-	-	-
Measured (µg)												
F1	40	21	29	4	32	49	24	61	11	8	7	1
F2	2	1	8	0	6	71	8	112	50	1	92	0
F3	44	44	34	14	47	356	37	235	279	42	285	28
TOTAL	86	66	71	18	85	476	59	408	340	51	384	29

Percent Recovery	C	C	C	Q	C	Q
F1	40	29	32	10	24	12
F2	2	8	6	14	8	22
F3	44	34	47	71	27	47
TOTAL	86	71	85	95	59	81

The results are disappointing in that only about half of the chrysotile recovered is associated with the separated sample, with most of the remainder associated with the initial alcohol washings of the reagent treated material. Recoveries of chrysotile range from 59 to 86 percent, averaging 75 percent. The quartz is also mainly present in the separated sample, with little evidence for selective separation of the chrysotile.

In the case of the serpentine rock sample (M15) initial quantities of 1.0 and 1.1 mg estimated to contain 1.8 percent chrysotile would be expected to yield 18 and 20 μg of chrysotile, respectively. In fact, much larger quantities are indicated, most of which is present in the settled sample. To determine the nature of this particulate matter, SEM photographs were obtained from samples 15A-F2, 15A-F3 and 15B-F3; these are reproduced in Figures 9 and 10, all at 1000X. The particles are mostly granular or platy with no evidence for chrysotile fibers in any of the samples. It cannot be ascertained whether there was any decoration of the serpentine rock particles by the AgI reagent thereby enhancing the quantity of particles in the settled sample.

On the basis of these results, it is concluded that there is no enhanced fractionation of chrysotile fibers by reagent treatment and high density liquid separation as practiced herein. As a result, no further experiments were conducted.

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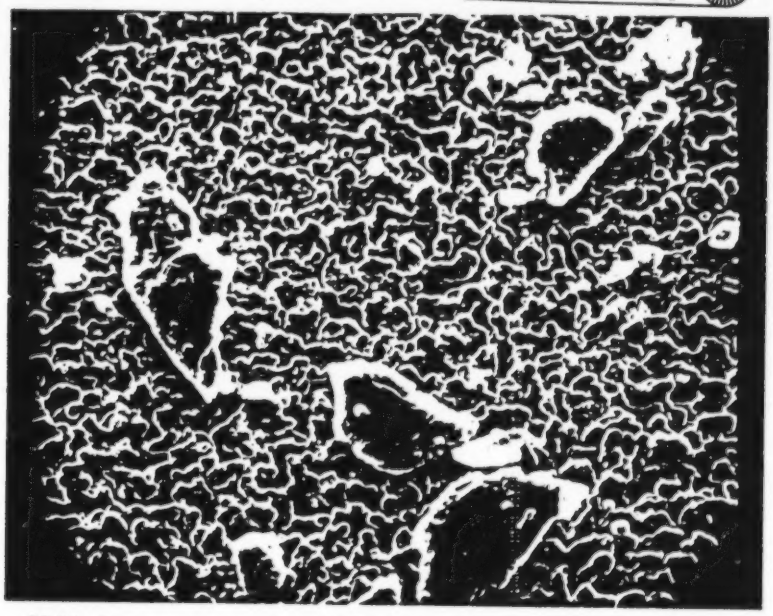
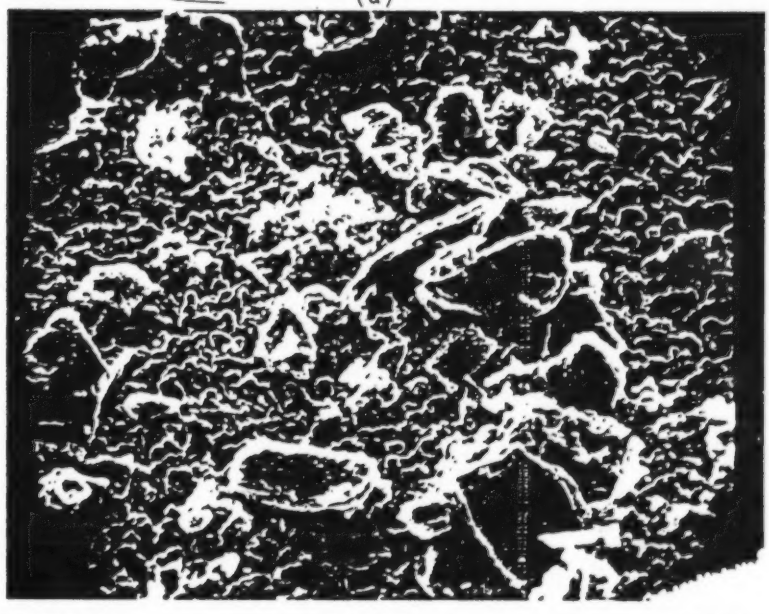


3580-2 15A-F2 1000X

(a)



3579-2 15A-F3 1000X

(b)

Figure 9. SEM photographs of particles in separated fractions of Sample M15A.
(a) Supernate (F2), (b) Settled solids (F3)

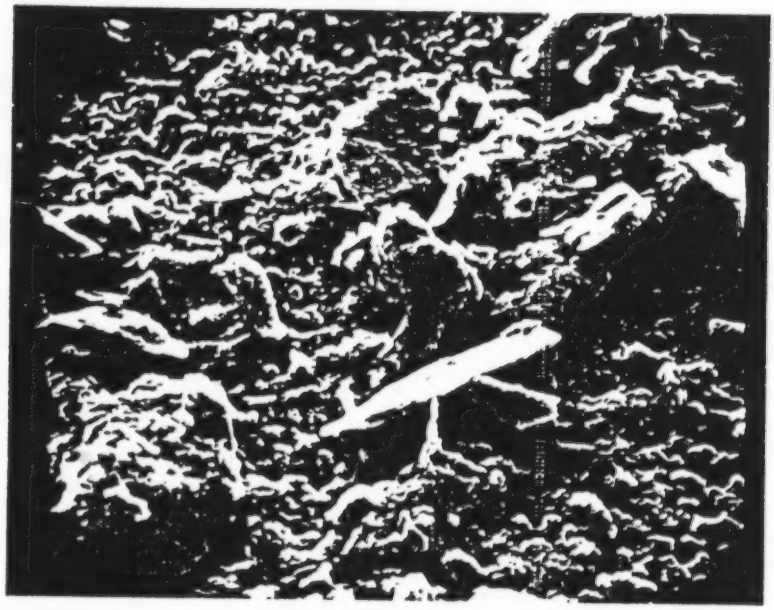


Figure 10. SEM photographs of particles in selected solids fraction of Sample M15B.

REFERENCES

1. Samudra, A.V., C.F. Harwood and J.D. Stockham. Electron Microscope Measurement of Airborne Asbestos Concentrations: A Provisional Methodology Manual. EPA-600/2-77-178, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1977.

2. Birks, L.S., M. Fatemi, J.V. Gilfrich and E.T. Johnson. Quantitative Analysis of Airborne Asbestos by X-ray Diffraction. EPA-650/2-75-004, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1975.

3. Fatemi, M., E.T. Johnson, R.R. Whitlock, L.S. Birks and J.V. Gilfrich. X-ray Analysis of Airborne Asbestos; Interim Report: Sample Preparation. EPA-600/2-77-062, 1977.

4. Birks, L.S., J.V. Gilfrich and J.W. Sandelin. X-ray Analysis of Airborne Asbestos; Final Report: Design and Construction of a Prototype Asbestos Analyzer. EPA-600/2-78-194, 1978.

5. Vonnegut, B., Science 116, 300, 1952.

6. Crystal Data, Determinative Tables, Second Ed., Donnay et al.

7. Speil, S. and J.P. Leinweber. Asbestos Minerals in Modern Technology. Environmental Research, 2, 166, 1969.